



Research paper

Spinel structured $\text{Co}_a\text{Mn}_b\text{O}_x$ mixed oxide catalyst for the selective catalytic reduction of NO_x with NH_3



Dongmei Meng, Qian Xu, Yunlei Jiao, Yun Guo, Yanglong Guo, Li Wang, Guanzhong Lu*, Wangcheng Zhan*

Key Laboratory for Advanced Materials and Research Institute of Industrial Catalysis, School of Chemistry and Molecular Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai, 200237, PR China

ARTICLE INFO

Keywords:

Mixed oxide
Selective catalytic reduction
Spinel structure
Thermal stability
Synergistic effect

ABSTRACT

A highly efficient catalyst of a $\text{Co}_a\text{Mn}_b\text{O}_x$ mixed oxide prepared by the co-precipitation method was developed for the selective catalytic reduction (SCR) of NO_x with ammonia. With an increase in the Mn content, the catalytic activity of the $\text{Co}_a\text{Mn}_b\text{O}_x$ mixed oxide exhibited a volcano-type tendency, and when Co/Mn molar ratio reached 7:3 ($\text{Co}_7\text{Mn}_3\text{O}_x$), the operation temperature for achieving > 80% NO_x conversion was 170 °C (116–285 °C window). The formation of spinel structured MnCo_2O_4 is highly important, and the presence of the spinel structure in $\text{Co}_7\text{Mn}_3\text{O}_x$ contributes to the increase in active sites and thermal stability and promotes SO_2 and/or H_2O resistance. In comparison with MnO_x or CoO_x alone, the $\text{Co}_a\text{Mn}_b\text{O}_x$ catalysts possess improved redox properties and more surface acid sites due to synergistic effects between the Co and Mn species. Among the $\text{Co}_a\text{Mn}_b\text{O}_x$ catalysts with different Co/Mn molar ratios, a higher NH_3 and $\text{NO} + \text{O}_2$ adsorption ability was found for the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst, originating from its $\text{MnCo}_2\text{O}_{4.5}$ phase and higher surface area, which leads to the higher activity of the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst. In situ DRIFTS indicated that bridging nitrate and bidentate nitrate are the intermediate species in the NH_3 -SCR reaction, and the high NO adsorption ability and improved redox properties of the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst are beneficial for the formation of nitrate species on the catalyst surface. Furthermore, NH_3 species adsorbed at Lewis acid sites taken part in SCR reaction, while the reactivity of NH_3 species adsorbed at Brønsted acid was not definitized.

1. Introduction

The emission of nitrogen oxides generated by power stations and mobile resources is regarded as a dominant contributor to atmospheric pollution [1,2], which can cause haze and acid rain, boost the photochemical chain reaction to form photochemical smog, aggravate the greenhouse effect, and injure the human respiratory system. Therefore, the control of NO_x emission has already attracted the world's attention. Consequently, many countries have established various standards to control NO_x emissions from power stations and mobile resources.

The selective catalytic reduction of NO_x with NH_3 (NH_3 -SCR) has been regarded as an efficient approach to eliminate NO_x in the presence of excess oxygen [3]. Many types of catalysts have been studied for the NH_3 -SCR reaction, among which commercially available vanadium-based mixed oxides and transition metal-exchanged zeolite catalysts are more widely used. Although vanadium-based SCR catalysts show high performance at 300–400 °C [4,5], they have some inherent disadvantages in practical applications, such as the narrow operation

temperature window, the high conversion of SO_2 to SO_3 at high temperatures and the toxicity of vanadium pentoxide to the environment and human health. Transition metal-exchanged zeolites [6–8] usually exhibit a wide operation temperature window at 250–600 °C and satisfactory de- NO_x efficiency. However, their hydrothermal stability is a great challenge for the large-scale application of zeolite-based catalysts. What is worse, when treating stack gases from stationary sources (accounting for approximately 46% of NO_x emission [9]), the gas temperature is usually low after passing through the sweetener and dust separation plant to eliminate SO_x and solid particles in the stack gases. Therefore, the study of SCR catalysts with excellent performance at low temperature (< 250 °C) has attracted much attention [10,11].

Some transition metal oxides have been proven to be effective for low-temperature NH_3 -SCR, especially manganese-based catalysts [12–14]. However, the catalytic activity of manganese oxides decreases dramatically at higher temperatures [15], where its structure, shape, valence state and surface area are changed, leading to a decrease in its catalytic activity for the NH_3 -SCR reaction [16,17]. As is well known,

* Corresponding authors.

E-mail addresses: gzhlu@ecust.edu.cn (G. Lu), zhanwc@ecust.edu.cn (W. Zhan).

perovskite, spinel and pyrochlore are typical structures of metal oxides with high stability. Since the low surface area of perovskite and pyrochlore is the most fatal disadvantage in the NH_3 -SCR reaction, we used spinel structured oxide as the catalyst for NH_3 -SCR. The introduction of a secondary element into transition metal oxides can modulate the ionic properties of the metal and increase the amount of surface defects on the oxides, thus promoting the efficiency of the transition metal oxide for the catalytic abatement of NO_x in the NH_3 -SCR reaction with acid and redox cycles. Previous research has revealed that Co-Mn mixed oxides exhibit good redox ability and high catalytic activity in oxidative reactions, such as CO oxidation, HC and VOC combustions [18–20], which is a very important factor for NH_3 -SCR. To promote the catalytic performance and simultaneously weaken the high-temperature sensitivity of manganese-based catalysts, spinel structured Co-Mn mixed oxides have great potential for development as a result of synergistic effects between manganese and cobalt, due to the high activity of Co_3O_4 for the NH_3 -SCR reaction [17] and the similar ionic radii of Co and Mn ($\text{Co}^{3+} = 0.63 \text{ \AA}$, $\text{Co}^{2+} = 0.72 \text{ \AA}$, $\text{Mn}^{4+} = 0.60 \text{ \AA}$ and $\text{Mn}^{3+} = 0.66 \text{ \AA}$).

Herein, spinel structured $\text{Co}_a\text{Mn}_b\text{O}_x$ catalysts were synthesized by the co-precipitation method, and the effects of the Co/Mn molar ratio on the structure and physicochemical properties and the catalytic performances of $\text{Co}_a\text{Mn}_b\text{O}_x$ mixed oxides for low-temperature NH_3 -SCR were systematically investigated by various characterization methods. Meanwhile, NH_3 -TPD, NO -TPD and in situ DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) were used to reveal the adsorption of reactants and the surface reactions of the adsorbed reactants. Subsequently, the mechanism of NH_3 -SCR over the $\text{Co}_a\text{Mn}_b\text{O}_x$ catalyst and the synergetic catalytic effect between the Mn and Co cations were explicitly discussed.

2. Experimental

2.1. Catalyst preparation

The $\text{Co}_a\text{Mn}_b\text{O}_x$ catalysts were synthesized by the co-precipitation method. MnSO_4 and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were used as salt precursors, and Na_2CO_3 solution was utilized as the precipitant. Typically, the desired amount of MnSO_4 and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 100 mL of deionized water at room temperature. Then, this mixed solution and a 0.2 M Na_2CO_3 solution were added dropwise to a beaker at the same time under stirring, and the pH value of the system was maintained at 9. After being stirred for 24 h, the solid product was collected by filtration, dried at 120°C for 12 h, and finally calcined in air at 550°C for 4 h at a heating rate of $2^\circ\text{C}/\text{min}$. All prepared catalysts were designated $\text{Co}_a\text{Mn}_b\text{O}_x$, where a/b is the ideal relative molar ratio of Co/Mn. For example, 2.26 g of MnSO_4 and 10.18 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was employed when producing $\text{Co}_7\text{Mn}_3\text{O}_x$. In addition, CoO_x and MnO_x samples were prepared using the same method without the addition of the second metal.

A Co-Mn mixed oxide catalyst (Co/Mn mole ratio was the same as $\text{Co}_7\text{Mn}_3\text{O}_x$) was also prepared by a two-step precipitation method as follows. 10.18 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 2.26 g of MnSO_4 were dissolved in 50 mL of deionized water separately. $\text{Co}(\text{NO}_3)_2$ solution and 0.2 M NaCO_3 solution were slowly added dropwise to a beaker with 100 mL of water, and the pH value was kept at 9. After stirring for 2 h, the MnSO_4 solution was added dropwise to the above precipitated solution along with a 0.2 M NaCO_3 solution. The following preparation process was the same as that for preparing the $\text{Co}_a\text{Mn}_b\text{O}_x$ catalysts, and the obtained catalyst was denoted $\text{CoO}_x/\text{MnO}_x$. Meanwhile, a Co-Mn mixed oxide was prepared in reverse order, i.e., MnSO_4 solution and 0.2 M NaCO_3 solution were precipitated first and then $\text{Co}(\text{NO}_3)_2$ solution was added into the above mixture along with a 0.2 M NaCO_3 solution. The obtained catalyst was denoted $\text{MnO}_x/\text{CoO}_x$.

2.2. Catalyst characterization

The XRD measurement was conducted on a Brook/D8 diffractometer employing Cu K α radiation. The diffraction patterns were obtained in the 2θ range of 10 – 80° with a step size of 0.06° . The crystalline phase was confirmed through comparison with the reference data from ICDD files. Transmission electron microscopy (TEM) of the samples was carried out on a JEOL 2100F electron microscope operated at 200 kV. The N_2 adsorption-desorption isotherms were measured on a Micromeritics ASAP 2020 M surface area and pore size analyzer. Before the measurements, all samples were degassed at 180°C until a stable vacuum of ca. 5 mTorr was reached. The specific surface area was calculated from desorption data by the Brunauer-Emmett-Teller (BET) method. The XPS spectra were obtained on a Thermo ESCALAB 250 spectrometer with Al K α radiation. The C 1 s line at 284.6 eV from contaminant carbon was defined as the reference.

The temperature-programmed desorption of NH_3 (NH_3 -TPD) was conducted on a PX200 apparatus (Tianjin Pengxiang Technology Limited Corporation) with a thermal conductivity detector (TCD). For this, 100 mg of catalyst was added to the quartz reactor and then pre-treated at 450°C in a flow of N_2 (50 mL/min) for 1 h. When being cooled to room temperature, the sample was exposed to a flow of 10% NH_3/N_2 (50 mL/min) for 1 h. After the sample was flushed with N_2 (50 mL/min) for 1 h, NH_3 -TPD was carried out at a heating rate of $10^\circ\text{C}/\text{min}$ in N_2 (50 mL/min) from room temperature to 450°C .

The O_2 -TPD-MS experiment was implemented on an automatic chemical adsorption instrument (Micromeritics Autochem ii 2920) equipped with a U-shaped quartz reactor and a mass spectrometer (HIDEN HPR 20). For this, 50 mg of sample was pretreated at 250°C in He for 30 min and in 3% O_2/He for another 30 min consecutively and then cooled down to 30°C in 3% O_2/He . After the catalyst was kept in He for 1 h, O_2 -TPD was run from 30°C to 600°C at a rate of $10^\circ\text{C}/\text{min}$.

The temperature-programmed desorption of NO_x (NO_x -TPD) was performed on custom-made equipment with an NO_x analyzer (Thermo Fisher 42i-HL- NO - NO_x analyzer) as the detector. The sample was pre-treated in 5 vol.% O_2/Ar (300 mL/min) at 450°C for 1 h and then cooled to room temperature. Then, the sample was exposed to a flow of 500 ppm $\text{NO}/5$ vol.% O_2/Ar (300 mL/min) for 1 h (when the NO_x on the samples reached a saturated state), followed by Ar (300 mL/min) purge for 1 h. Finally, TPD was run by heating the sample in Ar (300 mL/min) from room temperature to 450°C at $10^\circ\text{C}/\text{min}$.

Temperature-programmed reduction of H_2 (H_2 -TPR) experiments were also conducted on a PX200 apparatus with a TCD. For this, 50 mg of sample was directly heated from room temperature to 600°C at a rate of $10^\circ\text{C}/\text{min}$ in a flow of 5 vol.% H_2/N_2 (45 mL/min). The hydrogen consumption was quantitatively evaluated by the TCD signal.

In situ DRIFT measurements were performed on a Nicolet 6700 FT-IR spectrometer with an MCT detector. In the DRIFT cell, containing ZnSe windows and a connected gas flow system, the sample was pre-treated at 450°C in 5 vol.% O_2/Ar for 1 h and then cooled to 20°C in Ar. The background spectra were collected at certain temperatures during the cooling process, and these background spectra was subtracted from sample spectra accordingly.

2.3. Catalytic activity testing

The catalytic performances of the catalysts for NH_3 -SCR were detected in a continuous-flow fixed-bed quartz reactor at atmospheric pressure. For this, 300 mg of the catalyst (40–60 mesh) was used, and the reactant gas included 500 ppm NO , 500 ppm NH_3 , 5 vol.% H_2O (when used), 5 vol.% O_2 and Ar as the balanced gas. The gas hourly space velocity (GHSV) was $80,000 \text{ h}^{-1}$. The concentrations of NO and NO_2 in the gas mixture before and after the reaction were analyzed using the NO_x analyzer (Thermo Fisher 42i-HL- NO - NO_x analyzer). Because the oxidation of ammonia in the chamber of the NO/NO_x analyzer may cause an unexpected generation of NO_x , an ammonia trap

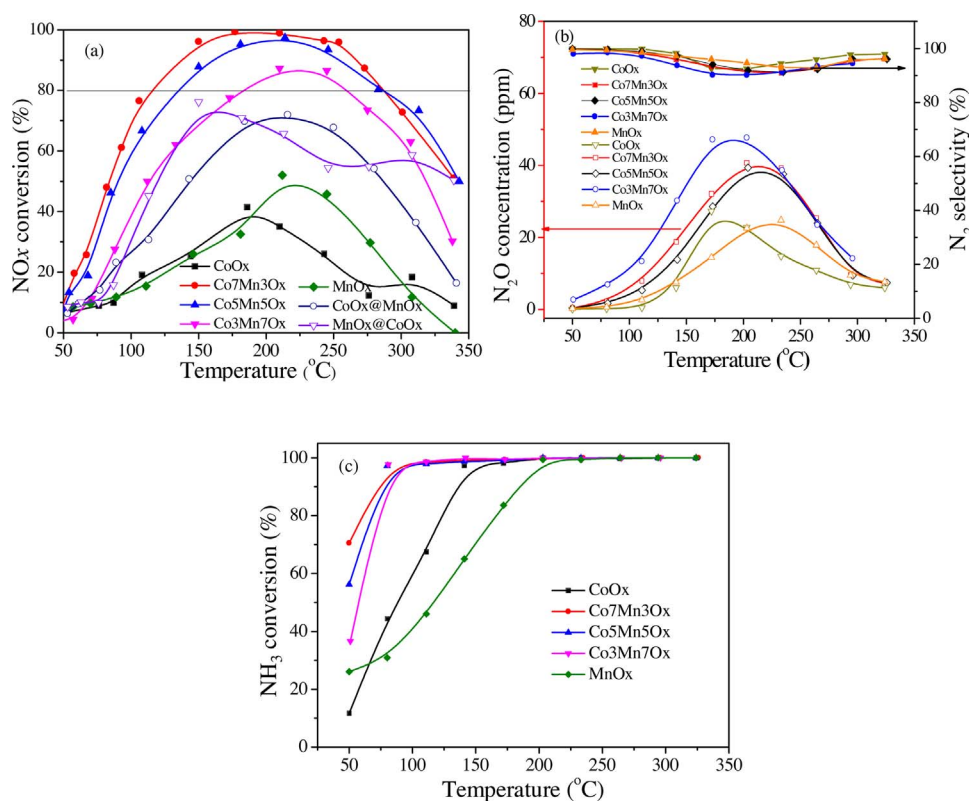


Fig. 1. Catalytic performances of the MnO_x, CoO_x, Co-Mn-O_x, Mn-Co-O_x and Co₃Mn₅O_x catalysts for the NH₃-SCR reaction, including NO_x conversion (a), N₂ selectivity along with N₂O concentration (b), as well as NH₃ conversion (c), as a function of temperature. (Reaction conditions: 0.3 g of sample, 500 ppm NO + 500 ppm NH₃ + 5 vol.% H₂O + 5 vol.% O₂/Ar balanced, total flow rate 300 mL/min and GHSV = 80000 h⁻¹).

containing phosphoric acid solution was installed prior to the analyzer. N₂O and NH₃ were monitored by a Nicolet 6700 FT-IR spectrometer with an MCT detector. NO_x conversion ($x(\text{NO}_x)$) and N₂ selectivity ($S(\text{N}_2)$) were calculated as follows:

$$x(\text{NO}_x) = \frac{C(\text{NO}_x)_{\text{in}} - C(\text{NO}_x)_{\text{out}}}{C(\text{NO}_x)_{\text{in}}} \times 100\%$$

$$S(\text{N}_2) = \frac{C(\text{NO}_x)_{\text{in}} + C(\text{NH}_3)_{\text{in}} - C(\text{NO}_x)_{\text{out}} - C(\text{NH}_3)_{\text{out}} - 2C(\text{N}_2\text{O})_{\text{out}}}{C(\text{NO}_x)_{\text{in}} + C(\text{NH}_3)_{\text{in}} - C(\text{NO}_x)_{\text{out}} - C(\text{NH}_3)_{\text{out}}} \times 100\%$$

$C(\text{NO}_x)_{\text{in}}$ and $C(\text{NO}_x)_{\text{out}}$ are the concentrations of NO_x in the inlet and outlet, respectively. $C(\text{NH}_3)_{\text{in}}$ and $C(\text{NH}_3)_{\text{out}}$ are the concentrations of NH₃ in the inlet and outlet, respectively. $C(\text{N}_2\text{O})$ is the concentration of N₂O generated during the reaction process.

3. Results and discussion

3.1. Effect of the Co/Mn molar ratio on the catalytic activity

Fig. 1a shows NO_x conversion as a function of temperature in the NH₃-SCR reaction over the MnO_x, CoO_x and Co₃Mn₅O_x catalysts. A bimodal curve of NO_x conversion with NO_x conversions of 41% (at 185 °C) and 18% (at 305 °C) can be observed over the CoO_x catalyst. Compared with CoO_x, MnO_x showed higher activity, over which ~54% NO_x conversion was achieved at 223 °C. However, the combination of Mn and Co to form a mixed oxide can dramatically enhance the NH₃-SCR catalytic performance, which is dependent on the Co/Mn molar ratio. When the molar ratio of Co/Mn is 7/3, the Co₇Mn₃O_x catalyst showed the best NH₃-SCR activity with an operation temperature window (80% NO_x conversion) of 116–285 °C, which is much better than the catalysts with Co/Mn molar ratios of 5/5 and 3/7. Additionally, the activity of the Co₇Mn₃O_x catalyst is also much higher than that of the CoO_x@MnO_x and MnO_x@CoO_x catalysts with the same Co/Mn molar ratio, which were prepared by the two-step precipitation method, indicating that the existence of synergistic effects between Co

and Mn oxide in the Co₇Mn₃O_x catalyst can obviously increase the catalytic activity of both MnO_x and CoO_x. N₂ selectivity along with the N₂O concentration, and NH₃ conversion as a function of temperature were also provided in Fig. 1b and c. All catalysts exhibited a high N₂ selectivity in the temperature range of 50–325 °C. However, N₂O concentration showed a volcano-type tendency over all catalysts and it reached the maximum at about 200 °C. Furthermore, the highest value of N₂O concentration decreased in the order of Co₃Mn₇O_x > Co₇Mn₃O_x > Co₅Mn₅O_x > CoO_x ≈ MnO_x. As for NH₃ conversion, it can reach 100% at 75 °C over the Co₃Mn₇O_x catalysts, indicating a high utilization of NH₃ for SCR reaction at low temperature. On the contrary, the temperature for NH₃ conversion of 100% increased to 200 °C over the CoO_x and MnO_x catalysts, due to their low catalytic activity for SCR reaction at low temperature, as shown in Fig. 1a.

The SCR activity is further studied to obtain information on the reaction kinetics, in which the NO_x conversion is less than 20%. The energy barrier and Arrhenius plot are presented in Fig. 2. It can be found that the rate constant increased in the order of MnO_x < Co₃Mn₇O_x < Co₅Mn₅O_x < Co₇Mn₃O_x, and the apparent energy barrier of Co₃Mn₇O_x (19.3 kJ/mol), Co₅Mn₅O_x (18.8 kJ/mol) and Co₇Mn₃O_x (15.7 kJ/mol) are significantly lower than that of MnO_x (33.9 kJ/mol) and CoO_x (24.3 kJ/mol). These results showed that the energy barrier of MnO_x and CoO_x was greatly changed after a second element was introduced, meaning that the active sites formed on these catalysts may be altered.

Meanwhile, the effect of calcination temperature of MnO_x and Co₇Mn₃O_x catalysts on their NH₃-SCR activity was also detected. As shown in Fig. 3, when increasing the calcination temperature of MnO_x from 450 to 650 °C, the highest NO_x conversion decreased from 97% over MnO_x-450 to 27% over MnO_x-650. Although the NH₃-SCR activity of the Co₇Mn₃O_x catalyst also decreased when increasing the calcination temperature, more than 80% NO_x can be removed in the operation temperature window ranged from 160 to 254 °C over the Co₇Mn₃O_x-650 catalyst. This results indicated that the Co₇Mn₃O_x catalyst exhibited a higher thermal stability in the NH₃-SCR reaction compared

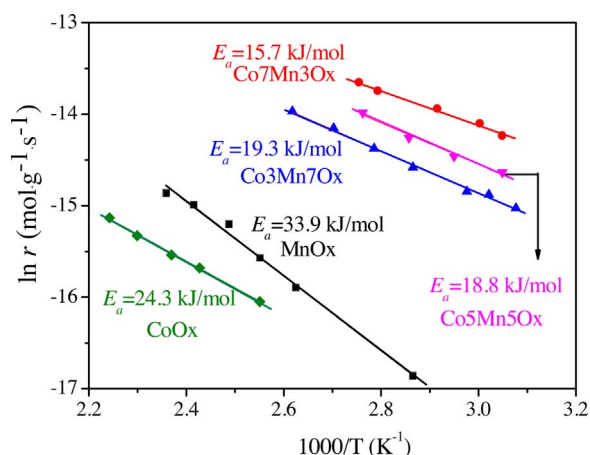


Fig. 2. Arrhenius plot for the NH_3 -SCR over the MnO_x -550, CoO_x -550 and $\text{Co}_3\text{Mn}_3\text{O}_x$ -550 catalysts.

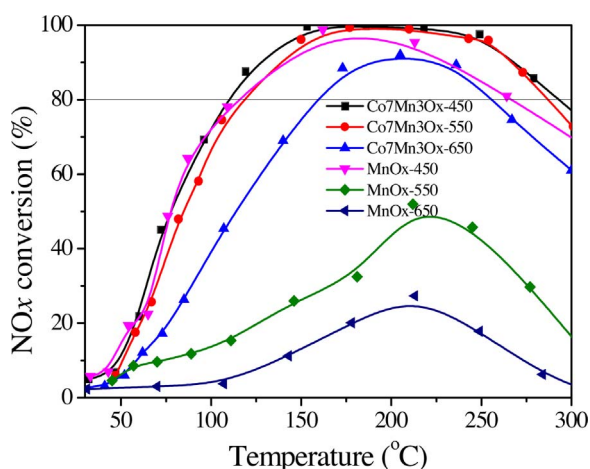


Fig. 3. NO_x conversion as a function of temperature in the NH_3 -SCR reaction over the $\text{Co}_7\text{Mn}_3\text{O}_x$ and MnO_x catalysts calcined at different temperature. (Reaction conditions: 0.3 g of sample, 500 ppm NO + 500 ppm NH_3 + 5 vol.% H_2O + 5 vol.% O_2 /Ar balanced, total flow rate 300 mL/min and GHSV = 80000 h^{-1}).

with MnO_x , which has a beneficial effect on the practical application of the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst.

On the other hand, to emphasize the advantages of the prepared catalysts, a series of catalysts for industrial applications, such as vanadium based catalysts and Cu-based zeolites, were considered as benchmark catalysts to compare the NH_3 -SCR activity, and their activity is directly extracted from the references. As shown in Fig. S1, the prepared $\text{Co}_3\text{Mn}_3\text{O}_x$ catalysts behaved a high NH_3 -SCR activity at low temperature and under a high space velocity, while vanadium based catalysts and Cu-based zeolites exhibited a wider temperature window for NO_x removal. Furthermore, the $\text{Co}_7\text{Mn}_3\text{O}_x$ -550 catalyst exhibited a wider temperature window for NO_x removal at the low temperature, compared with those reported Mn-based catalysts, as shown in Fig. S2.

3.2. Effect of SO_2 on the SCR reaction

As required for the practical use of NH_3 -SCR catalysts, water and SO_2 inevitably exist in the tail gas of power stations, which may quickly poison the catalyst. Fig. 4 displays the effect of H_2O and SO_2 on the activity of the MnO_x , $\text{Co}_3\text{Mn}_7\text{O}_x$ and $\text{Co}_7\text{Mn}_3\text{O}_x$ catalysts for the SCR reaction. The catalyst was kept under the reaction conditions for 4 h, and then 5 vol.% H_2O was introduced into the feed gas mixture for 8 h. After that, the reaction gas atmosphere was reset to ideal conditions for 2 h, followed by a reaction atmosphere including 50 ppm SO_2 . As

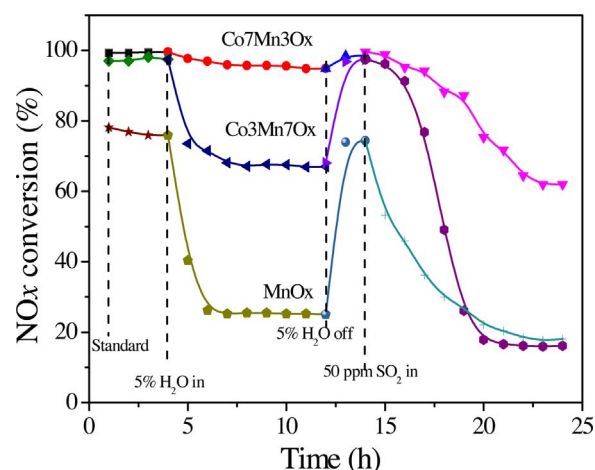


Fig. 4. Effect of water and SO_2 on the catalytic activities of the MnO_x , $\text{Co}_3\text{Mn}_7\text{O}_x$ and $\text{Co}_7\text{Mn}_3\text{O}_x$ catalysts for the SCR reaction. (Reaction conditions: 0.3 g sample; 180 $^\circ\text{C}$; 500 ppm NO + 500 ppm NH_3 + 5 vol.% O_2 + 5 vol.% H_2O (when used) + 50 ppm SO_2 (when used)/Ar balanced, total flow rate 300 mL/min and GHSV = 80000 h^{-1}).

shown in Fig. 4, when 5 vol.% H_2O is introduced into the feed gas, NO_x conversion decreases drastically to 25% and 67% over the MnO_x and $\text{Co}_3\text{Mn}_7\text{O}_x$ catalysts, respectively. However, NO_x conversion remains greater than 95% over the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst during the same period, indicating that the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst possesses excellent water-resistance performance. At the same time, the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst exhibits excellent sulfur-resistance performance. The high activity with 62% NO_x conversion can be maintained over the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst after poisoning by the feed gas that includes 50 ppm SO_2 for 10 h, whereas the other two samples are almost deactivated completely. Furthermore, even if 5% H_2O and 50 ppm SO_2 were introduced into the feed gas simultaneously, NO_x conversion over the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst is also much higher than that over the other two samples (Fig. S3), confirming a high water-resistance and sulfur-resistance performance of the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst. On the other hand, it is interesting that all the MnO_x , $\text{Co}_3\text{Mn}_7\text{O}_x$ and $\text{Co}_7\text{Mn}_3\text{O}_x$ catalysts can be regenerated simply by washing with water. As shown in Fig. 5, the catalytic activities of the catalysts can be recovered, and even the activities of the MnO_x and $\text{Co}_3\text{Mn}_7\text{O}_x$ catalysts are better than those of the fresh samples. As a result, regenerated $\text{Co}_3\text{Mn}_7\text{O}_x$ and $\text{Co}_7\text{Mn}_3\text{O}_x$ catalysts show the similar SCR activity. The reason for the decreased gap between the SCR activity of regenerated $\text{Co}_3\text{Mn}_7\text{O}_x$ and $\text{Co}_7\text{Mn}_3\text{O}_x$ catalysts compared with fresh

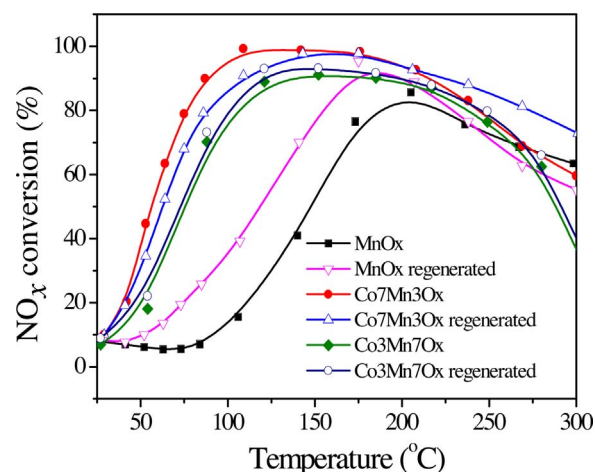


Fig. 5. Catalytic activities of the fresh and regenerated MnO_x , $\text{Co}_3\text{Mn}_7\text{O}_x$ and $\text{Co}_7\text{Mn}_3\text{O}_x$ catalysts for the SCR reaction. (Reaction conditions: 0.3 g of sample, 500 ppm NO + 500 ppm NH_3 + 5 vol.% O_2 /Ar balanced, total flow rate 300 mL/min and GHSV = 80000 h^{-1}).

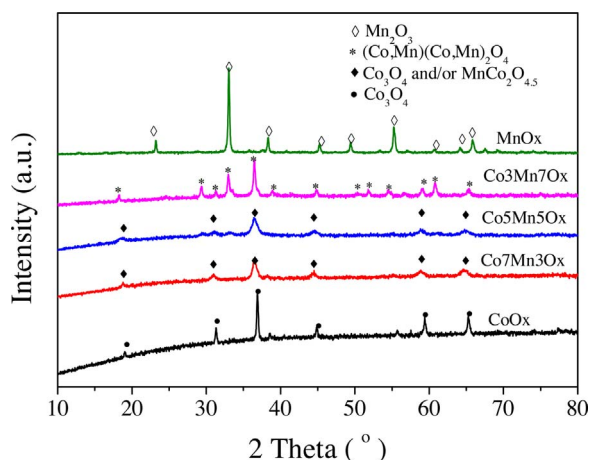


Fig. 6. XRD patterns of the $\text{Co}_a\text{Mn}_b\text{O}_x$ catalysts with different Co/Mn mole ratio.

catalysts may be the decrease in their activity for NO oxidation, which makes the catalytic activity of two catalysts for NO oxidation closer (Fig. S4).

3.3. Structural properties of the catalysts

Fig. 6 depicts the XRD patterns of the CoO_x , MnO_x and $\text{Co}_a\text{Mn}_b\text{O}_x$ catalysts with various Co/Mn molar ratios. In the XRD patterns of CoO_x and MnO_x , the diffraction peaks mainly represent spinel structured Co_3O_4 and Mn_2O_3 , respectively. The XRD patterns of the $\text{Co}_a\text{Mn}_b\text{O}_x$ catalysts vary with the Co/Mn molar ratio. The $\text{Co}_3\text{Mn}_7\text{O}_x$ catalyst presents diffraction peaks for well crystallized $(\text{Co}, \text{Mn})(\text{Co}, \text{Mn})_2\text{O}_4$, and the diffraction peaks of $\text{MnCo}_2\text{O}_{4.5}$ or Co_3O_4 are shown in the XRD patterns of the $\text{Co}_5\text{Mn}_5\text{O}_x$ and $\text{Co}_7\text{Mn}_3\text{O}_x$ catalysts [21,22]. Since the diffraction peaks of Co_3O_4 and $\text{MnCo}_2\text{O}_{4.5}$ are present at very similar 2θ angles and the Co/Mn molar ratio of the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst is higher than that of $\text{MnCo}_2\text{O}_{4.5}$, it is deduced that the diffraction peaks in the XRD pattern of the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst may overlap with the signals of Co_3O_4 and $\text{MnCo}_2\text{O}_{4.5}$. In contrast, the Co/Mn molar ratio of the $\text{Co}_5\text{Mn}_5\text{O}_x$ catalyst is lower than that of $\text{MnCo}_2\text{O}_{4.5}$, and the diffraction peaks of Mn_2O_3 do not appear in the XRD patterns of the $\text{Co}_5\text{Mn}_5\text{O}_x$ catalyst, indicating that some of the MnO_x may be homogeneously dispersed on the catalyst surface with the other species.

The Raman spectra of the catalysts are shown in Fig. 7. There are five peaks centered at 190, 466, 509, 605 and 674 cm^{-1} for the CoO_x catalyst, which are assigned to the F_{2g} , E_g , F_{2g} , F_{2g} and A_{1g} symmetries, respectively [23,24]. For the MnO_x catalyst, only a strong peak at 635 cm^{-1} existed, which was assigned to Mn_2O_3 with a distorted

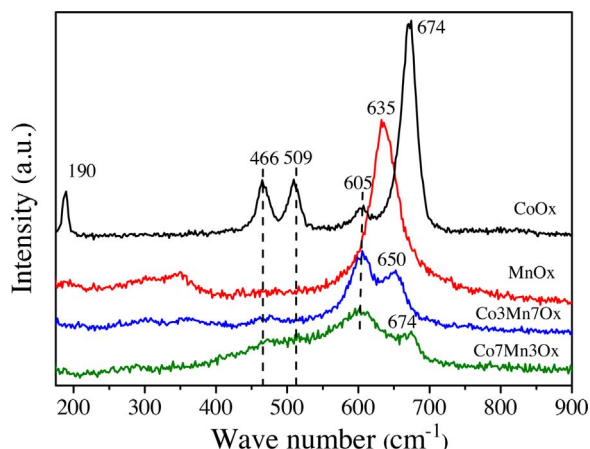


Fig. 7. Raman spectra of the CoO_x , MnO_x and $\text{Co}_a\text{Mn}_b\text{O}_x$ catalysts.

hausmannite structure [25–28]. The Raman spectra of the $\text{Co}_a\text{Mn}_b\text{O}_x$ catalysts are greatly different from those of CoO_x and MnO_x and depend on the molar ratio of Co/Mn in the catalysts. There are two strong peaks at 605 and 650 cm^{-1} assigned to MnO_2 and Mn_3O_4 species, respectively, in the Raman spectra of the $\text{Co}_3\text{Mn}_7\text{O}_x$ catalyst [28–30]. In contrast, the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst exhibits two strong peaks at 605 and 674 cm^{-1} assigned to MnO_2 and Co_3O_4 species, respectively. The presence of Co_3O_4 in the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst is also reflected in the XRD profiles. Finally, the lower Raman signal intensity of the cobalt-containing samples indicated the reduced crystallinity of these catalysts [31], which is consistent with the XRD results.

TEM images of the MnO_x , CoO_x , $\text{Co}_3\text{Mn}_7\text{O}_x$ and $\text{Co}_7\text{Mn}_3\text{O}_x$ catalysts are displayed in Fig. 8. The four samples exhibited similar irregular particles, and their sizes are ranked in the order of $\text{MnO}_x > \text{CoO}_x > \text{Co}_3\text{Mn}_7\text{O}_x > \text{Co}_7\text{Mn}_3\text{O}_x$. The sizes of the Co_3O_4 particles are mainly 30–80 nm, and the lattice spacing is 0.475 nm, which is assigned to the Co_3O_4 (111) facet. The MnO_x catalyst consisted of nanoparticles and nanorods, and the nanorods resulted from the adhesion or agglomeration of nanoparticles. The lattice spacings are 0.396 nm, 0.315 nm and 0.250 nm, which correspond to the Mn_2O_3 (211), (122) and (321) facets. However, several types of stripes are present on the $\text{Co}_3\text{Mn}_7\text{O}_x$ catalyst (Fig. 8C). Those with lattice spacings of 0.503 nm and 0.272 nm are ascribed to the $(\text{Co}, \text{Mn})(\text{Co}, \text{Mn})_2\text{O}_4$ (111) and (113) facets, and the lattice spacing of 0.390 nm is probably ascribed to the (211) facet of excess Mn_2O_3 that was formed. For the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst (Fig. 8D), the lattice spacings of 0.473 nm and 0.259 nm are attributed to the MnCo_2O_4 (111) and (311) facets. Compared with the particle size of $\text{Co}_3\text{Mn}_7\text{O}_x$ (15–50 nm), the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst exhibited a smaller size (6–30 nm), resulting in a larger specific surface area (Table 1).

Fig. 9 shows the O 1s, Co 2p and Mn 2p XPS spectra of the MnO_x , CoO_x , $\text{Co}_3\text{Mn}_7\text{O}_x$, $\text{Co}_5\text{Mn}_5\text{O}_x$ and $\text{Co}_7\text{Mn}_3\text{O}_x$ catalysts. In the O 1s XPS spectra, all catalysts exhibited two distinguishing peaks. The peak at B.E. = 529.0–529.8 eV is attributed to lattice oxygen (O_L), and the peak at 530.5–531.3 eV belongs to surface oxygen (O_S), including surface adsorbed oxygen (such as O_2^- or O^-) and that of hydroxyl-like groups [32]. The $\text{O}_S/(\text{O}_L + \text{O}_S)$ ratios of the catalysts were calculated and are shown in Table 1. The ratios of $\text{O}_S/(\text{O}_L + \text{O}_S)$ for the $\text{Co}_7\text{Mn}_3\text{O}_x$, $\text{Co}_5\text{Mn}_5\text{O}_x$, $\text{Co}_3\text{Mn}_7\text{O}_x$ and MnO_x catalysts are 32%, 33%, 43% and 42%, respectively, which is much lower than that of the CoO_x (63%) catalyst. In the Co 2p XPS spectra, the peaks at 779.4 ± 0.3 eV and 780.8 ± 0.1 eV are assigned to Co^{3+} and Co^{2+} , respectively [33]. The peak at 786.3 ± 0.1 eV is the satellite peak of Co 2p. As shown in Table 1, the $\text{Co}^{3+}/(\text{Co}^{2+} + \text{Co}^{3+})$ ratios for the $\text{Co}_7\text{Mn}_3\text{O}_x$, $\text{Co}_5\text{Mn}_5\text{O}_x$ and $\text{Co}_3\text{Mn}_7\text{O}_x$ catalysts are 42.6%, 56.2% and 44.3%, respectively, which is lower than that of the CoO_x catalyst (73.8%). In the Mn 2p XPS spectra, three peaks can be observed at 635–647 eV for all the catalysts. The peaks at 640.1 ± 0.4 and 641.6 ± 0.2 eV represent Mn^{3+} and Mn^{4+} , respectively [34], and the peak at 643.5 ± 0.3 eV is assigned to the satellite peak of Mn 2p [35]. As shown in Table 1, the atomic ratio of $\text{Mn}^{4+}/(\text{Mn}^{3+} + \text{Mn}^{4+})$ in the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst was 76.4%, which is much higher than that in the MnO_x (25.3%), $\text{Co}_3\text{Mn}_7\text{O}_x$ (64.4%) and $\text{Co}_5\text{Mn}_5\text{O}_x$ (53.4%) catalysts, probably due to the different MnCoO_x phases formed between the $\text{Co}_3\text{Mn}_7\text{O}_x$, $\text{Co}_5\text{Mn}_5\text{O}_x$ and $\text{Co}_7\text{Mn}_3\text{O}_x$ catalysts. As is well known, high concentrations of surface oxygen (O_S) and metal ions with high oxidation states (such as Mn^{4+} and Co^{3+}) on the catalyst surface are beneficial to the catalytic oxidation ability of this catalyst, which can enhance the oxidation of NO to NO_2 to accelerate the NH_3 -SCR reaction. Based on the XPS results, it is impossible to directly estimate or compare the oxidation ability of the MnO_x , $\text{Co}_3\text{Mn}_7\text{O}_x$, $\text{Co}_5\text{Mn}_5\text{O}_x$ and $\text{Co}_7\text{Mn}_3\text{O}_x$ catalysts because the changes in the parameters in relation to their oxidation ability are not uniform.

3.4. Reducibility and oxidizability of the catalysts

Fig. 10 shows the H_2 -TPR profiles of the CoO_x , MnO_x and $\text{Co}_a\text{Mn}_b\text{O}_x$

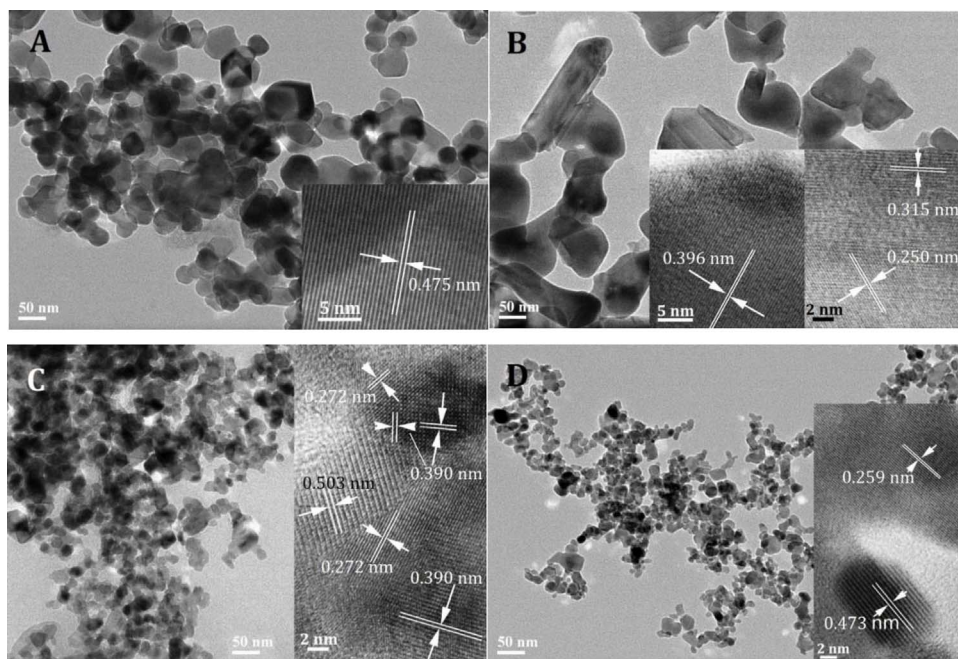


Fig. 8. TEM images of the CoO_x (A), MnO_x (B), $\text{Co}_3\text{Mn}_7\text{O}_x$ (C) and $\text{Co}_7\text{Mn}_3\text{O}_x$ (D) catalysts.

catalysts. The CoO_x catalyst exhibits two reduction peaks at 315 and 393 °C, which are ascribed to the reduction of $\text{Co}^{3+} \rightarrow \text{Co}^{2+}$ and $\text{Co}^{2+} \rightarrow \text{Co}$, respectively [36]. The MnO_x catalyst exhibits two reduction peaks at 346 and 441 °C, belonging to the reduction of $\text{MnO}_2/\text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4$ and $\text{Mn}_3\text{O}_4 \rightarrow \text{MnO}$, respectively [15,21,37–41,42]. However, three reduction peaks appeared in the H_2 -TPR profiles of all of the $\text{Co}_a\text{Mn}_b\text{O}_x$ catalysts. The α peak at 259–269 °C is ascribed to the reduction of MnO_2 to Mn_2O_3 [17,43], and the amount of H_2 consumption for the $\text{Co}_3\text{Mn}_7\text{O}_x$ catalyst is higher than that for the $\text{Co}_7\text{Mn}_3\text{O}_x$ and $\text{Co}_5\text{Mn}_5\text{O}_x$ catalysts, due to the higher amount of Mn^{4+} on the $\text{Co}_3\text{Mn}_7\text{O}_x$ surface. As shown in Table 1, although the atomic ratio of $\text{Mn}^{4+}/(\text{Mn}^{3+} + \text{Mn}^{4+})$ on the $\text{Co}_3\text{Mn}_7\text{O}_x$ surface is slightly lower than that on the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst, the Mn content in the $\text{Co}_3\text{Mn}_7\text{O}_x$ catalyst is much higher than that in the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst, resulting in more Mn^{4+} on the $\text{Co}_3\text{Mn}_7\text{O}_x$ surface. The β peak at 332–368 °C is assigned to the simultaneous reduction of $\text{Co}^{3+} \rightarrow \text{Co}^{2+}$ and $\text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4$, and the γ peak at 493 °C is assigned to the reduction of $\text{Co}^{2+} \rightarrow \text{Co}$ and $\text{Mn}_3\text{O}_4 \rightarrow \text{MnO}$. For the $\text{Co}_3\text{Mn}_7\text{O}_x$, $\text{Co}_5\text{Mn}_5\text{O}_x$ and $\text{Co}_7\text{Mn}_3\text{O}_x$ catalysts, the amount of H_2 consumption for the β peak is similar. However, the amount of H_2 consumption for the γ peak increased with increasing the Co amount in the $\text{Co}_a\text{Mn}_b\text{O}_x$ catalysts. On the other hand, the highest temperatures of α and β peaks for the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst are slightly lower than those for other two catalysts. In summary, the $\text{Co}_3\text{Mn}_7\text{O}_x$, $\text{Co}_5\text{Mn}_5\text{O}_x$ and $\text{Co}_7\text{Mn}_3\text{O}_x$ catalysts exhibit similar reducibility at low temperature (< 400 °C), but their reducibility is much better than those of the MnO_x and CoO_x catalysts.

The oxidation abilities of the catalysts were investigated by both the CO oxidation and O_2 -TPD techniques. The CO + O_2 reaction on the CoO_x , MnO_x and $\text{Co}_a\text{Mn}_b\text{O}_x$ catalysts was estimated and is shown in Fig. 11a. All of the CoO_x , MnO_x , $\text{Co}_3\text{Mn}_7\text{O}_x$ and $\text{Co}_7\text{Mn}_3\text{O}_x$ catalysts exhibited similar high catalytic activity, indicating that all of the catalysts showed similar oxidizability under CO oxidation conditions. In the O_2 -TPD-MS profiles (Fig. 11b), the desorption peaks below 250 °C can be ascribed to surface adsorbed oxygen, including O_2^- and O^- . Above this temperature, desorbed O species are attributed to lattice oxygen. In comparison with the catalysts containing low Mn amounts (CoO_x and $\text{Co}_7\text{Mn}_3\text{O}_x$), the catalysts containing high Mn amounts ($\text{Co}_3\text{Mn}_7\text{O}_x$ and MnO_x) have much more mobile lattice oxygen at > 250 °C.

To further investigate the reactivity and recovery of the lattice oxygen of the catalyst, alternating experiments of CO reduction and O_2 re-oxidation over the catalysts were run at 250 °C (the surface adsorbed oxygen can be removed at this temperature according to O_2 -TPD). As shown in Fig. 12, for the MnO_x catalyst, the formed CO_2 signal is the largest in the first CO reduction cycle; after the sample was re-oxidized for 5 min, the signal of the formed CO_2 decreased greatly in the second cycle, and CO was introduced; in the following repeated test of CO reduction- O_2 re-oxidation, similar results to the second run were obtained. This shows that a number of the lattice oxygen in MnO_x that were reduced by CO could not be recovered to their initial state in the fresh sample. Unlike the MnO_x sample, the first signal of formed CO_2 is almost the same as the subsequent CO_2 signals in $\text{Co}_7\text{Mn}_3\text{O}_x$, which means that the lattice oxygen consumed by CO reduction can be

Table 1
BET surface area (S_{BET}) and surface composition of $\text{Co}_a\text{Mn}_b\text{O}_x$ with different Co/Mn molar ratios.

Catalyst	S_{BET} (m^2/g)	Co/Mn (mol)		$\text{Co}^{3+}/(\text{Co}^{2+} + \text{Co}^{3+})^b$ (%)	$\text{O}_s/(\text{O}_L + \text{O}_s)^b$ (%)	$\text{Mn}^{4+}/(\text{Mn}^{4+} + \text{Mn}^{3+})^b$ (%)
		In bulk ^a	On surface ^b			
MnO_x	18	–	–	–	42	25.3
$\text{Co}_3\text{Mn}_7\text{O}_x$	20	0.44	0.26	44.3	43	64.4
$\text{Co}_5\text{Mn}_5\text{O}_x$	55	0.82	0.75	56.2	33	53.4
$\text{Co}_7\text{Mn}_3\text{O}_x$	51	2.33	2.29	42.6	32	76.4
CoO_x	10	–	–	73.8	63	–

^a Determined by the ICP analysis.

^b Calculated by the XPS data.

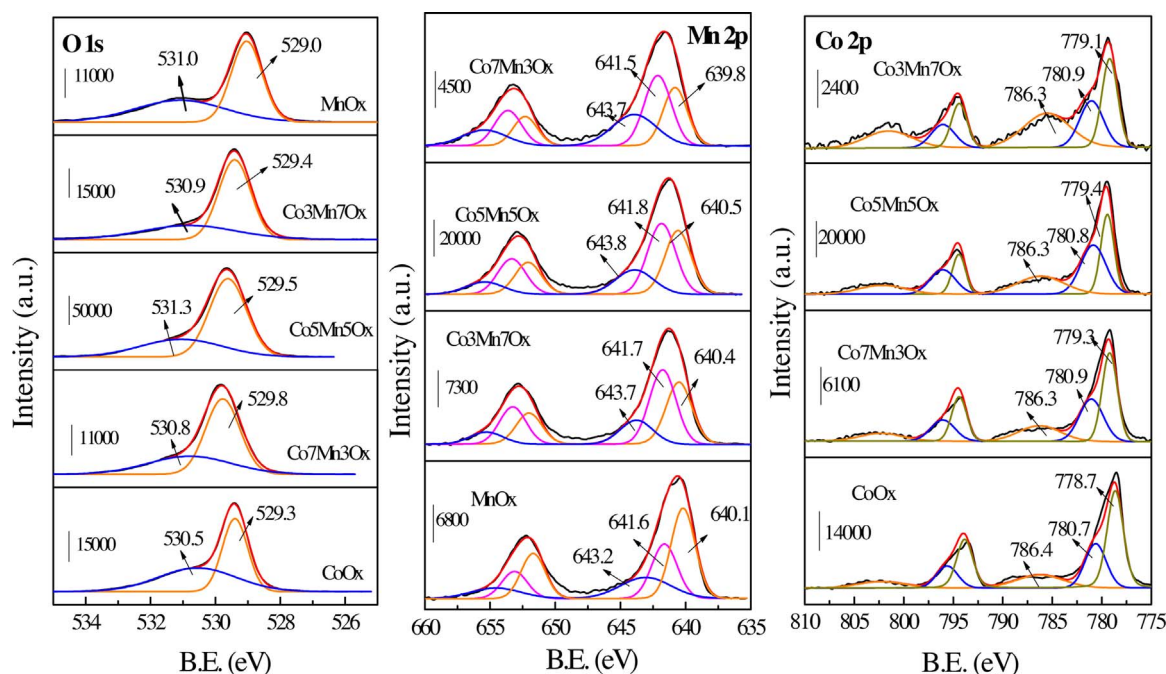


Fig. 9. O 1s, Co 2p and Mn 2p XPS spectra of the MnO_x , $\text{Co}_3\text{Mn}_7\text{O}_x$, $\text{Co}_5\text{Mn}_5\text{O}_x$, $\text{Co}_7\text{Mn}_3\text{O}_x$ and CoO_x catalysts.

recovered after 5 min of re-oxidation with gaseous oxygen. The results above show that $\text{Co}_7\text{Mn}_3\text{O}_x$ has better oxygen mobility than MnO_x , and consumed lattice oxygen can be quickly replenished by gaseous oxygen.

The ability for NH_3 adsorption is one of the deciding factors for NH_3 -SCR catalysts, thus the surface acidity of the catalyst is important for an excellent NH_3 -SCR catalyst. The NH_3 -TPD profiles of the CoO_x , MnO_x and $\text{Co}_a\text{Mn}_b\text{O}_x$ catalysts are shown in Fig. 13. In the NH_3 -TPD profile of MnO_x , there are mainly two overlapped desorption peaks at 80 and 180 °C, and for the CoO_x catalyst, three overlapped desorption peaks centered at 102, 180 and 315 °C can be observed. For the $\text{Co}_a\text{Mn}_b\text{O}_x$ catalysts, desorption peaks similar to those of the CoO_x and MnO_x catalysts can be observed, but their intensities are obviously improved by increasing the molar ratio of Co/Mn, where the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst possessed the highest amount of acid sites among all $\text{Co}_a\text{Mn}_b\text{O}_x$ catalysts. For the NH_3 -SCR reaction, whether the mechanism is Langmuir-Hinshelwood or Eley-Rideal, the increase in the amount of surface acid sites can enhance the adsorption of NH_3 and result in the

improvement of the NH_3 -SCR reaction [32,44]. Therefore, the high NH_3 adsorption ability of the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst is beneficial to its high catalytic activity in NH_3 -SCR.

Since the NH_3 adsorption amount may be affected by the surface area of the catalyst and NH_3 desorbing below 250 °C is considered effective for low-temperature NH_3 -SCR, the integrated areas of the desorption peaks at < 250 °C per unit surface area ($\text{Area}/S_{\text{BET}}$, a.u./m²) were calculated. The $\text{Area}/S_{\text{BET}}$ values ranked as follows: CoO_x (84.3) > $\text{Co}_3\text{Mn}_7\text{O}_x$ (66.4) > $\text{Co}_7\text{Mn}_3\text{O}_x$ (53.3) > MnO_x (41.3). The abovementioned results showed that the CoO_x catalyst exhibited stronger acidic properties and had more acidic sites at < 250 °C than the MnO_x catalyst. This means that the presence of Co in the $\text{Co}_a\text{Mn}_b\text{O}_x$ catalyst can increase the acidic properties and the NH_3 adsorption ability of MnO_x . For the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst, because its surface area is the largest among all catalysts and even 5 times greater than that of the CoO_x catalyst, it has the most acid sites among all the catalysts.

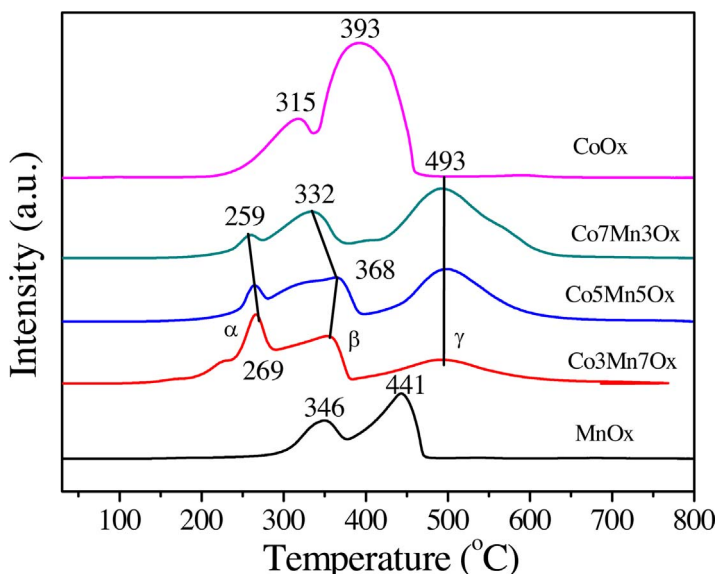


Fig. 10. H_2 -TPR profiles of the CoO_x , MnO_x and $\text{Co}_a\text{Mn}_b\text{O}_x$ catalysts.

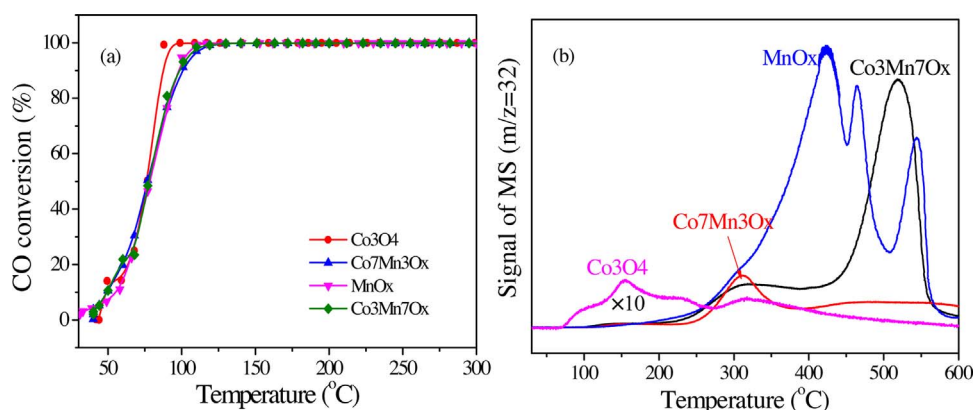


Fig. 11. (a) CO oxidation and (b) O₂-TPD-MS profiles over the CoO_x, MnO_x and Co₃Mn₇O_x catalysts. (CO oxidation conditions: 100 mg sample, 1%CO + 20% O₂/N₂ balanced with flow rate of 100 mL/min, GHSV = 60000 mL/g_{cat} h).

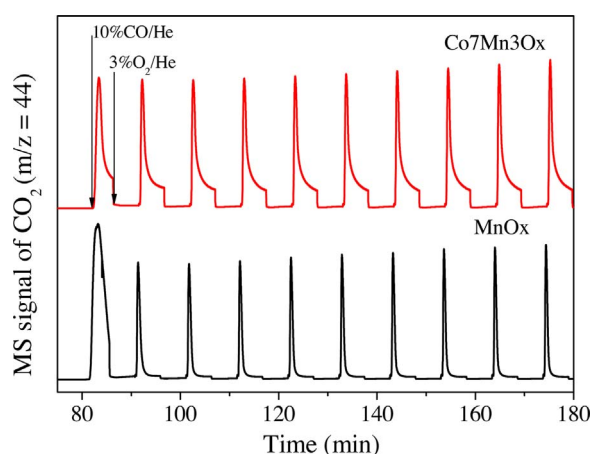


Fig. 12. Alternation experiments of CO reduction and O₂ re-oxidation over the Co₇Mn₃O_x-550 and MnO_x-550 samples at 250 °C. (Reaction conditions: 50 mg sample pre-treated in He at 250 °C for 60 min, 10%CO/He was passed the catalyst bed for 5 min, then 3% O₂/He was used to oxidize the catalyst for 5 min).

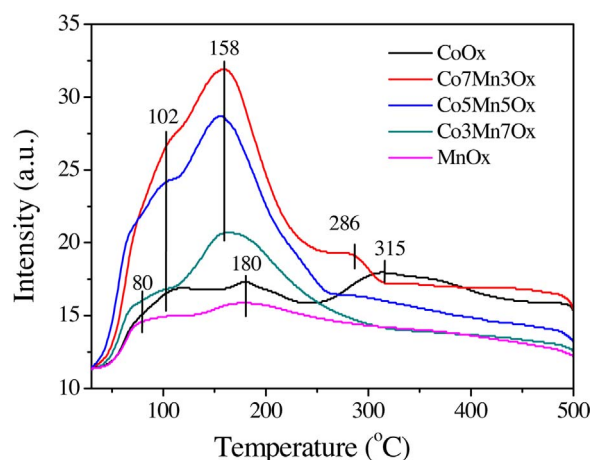


Fig. 13. NH₃-TPD profiles of the CoO_x, MnO_x and Co₃Mn₇O_x catalysts.

3.5. Catalytic activity for NO oxidation and adsorption ability for NO_x

It has been reported that a good SCR catalyst usually exhibits higher catalytic performance for NO oxidation, which is beneficial to the “fast SCR” reaction, $\text{NO} + \text{NO}_2 + 2\text{NH}_3 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}$. Therefore, the catalytic activities of the catalysts for NO oxidation were studied, as shown in Fig. 14. For NO oxidation at low temperature (< 200 °C), the Co₃Mn₇O_x catalysts exhibited similar catalytic activities, which are higher than those of the MnO_x and CoO_x catalysts. As shown in the H₂-

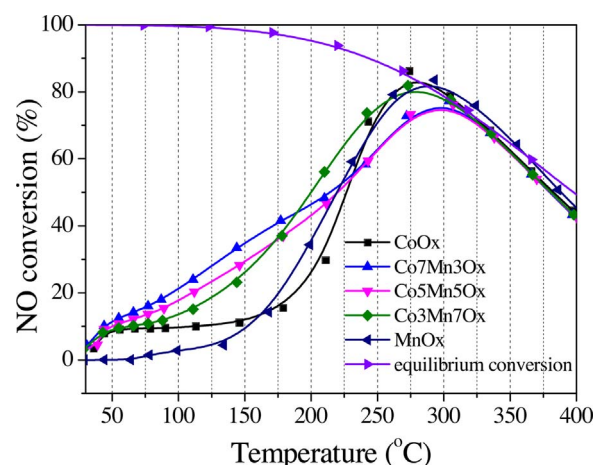


Fig. 14. NO oxidation over the CoO_x, MnO_x and Co₃Mn₇O_x catalysts. (Reaction conditions: 500 ppm NO + 5 vol.% O₂/Ar balanced, total flow rate 300 mL/min and GHSV = 80000 h⁻¹).

TPR profiles, the Co₃Mn₇O_x catalysts displayed similar reducibility at low temperature, which may be the reason for the similar activities of the Co₃Mn₇O_x catalysts for NO oxidation. Comparing the catalytic performance for NO oxidation with the SCR activity (Fig. 1), no direct correspondence between their catalytic activities for NO oxidation and the NH₃-SCR reaction can be observed. The reason may be that NO oxidation to NO₂ by oxygen is not the rate-determining step in the SCR reaction over these catalysts [11,45].

Fig. 15 shows the NO_x-TPD profiles of the CoO_x, MnO_x and Co₃Mn₇O_x catalysts after being treated in 500 ppm NO and 5% O₂/Ar for 1 h with a flow rate of 300 mL/min. The shape of the entire curve changed significantly with the varied composition of the catalyst, due to the different surface phases of Co₃Mn₇O_x in these catalysts. In the NO_x-TPD curves of all catalysts except MnO_x, there are three overlapped NO_x desorption peaks in the temperature range of 50–400 °C. The desorption peak at < 200 °C is attributed to physisorbed NO_x and decomposition of nitrite species, while the desorption peak at > 200 °C can be ascribed to the decomposition of bridged nitrate species and bidentate nitrate species with higher thermal stability [15,46–48]. Furthermore, the top temperatures of desorption peaks over the Co₇Mn₃O_x catalyst are different from that over the Co₃Mn₇O_x and Co₅Mn₅O_x catalysts, due to the difference in the interaction between nitrate/nitrite species and the surface of the Co₃Mn₇O_x catalysts composed with different MnO_x phases.

On the other hand, the amount of desorbed NO_x on the Co₇Mn₃O_x catalyst is much more than that on the MnO_x, CoO_x and Co₃Mn₇O_x catalysts and slightly more than that on the Co₅Mn₅O_x catalyst. The integrated areas of desorption peak per square meter of surface area (Area/S_{BET}) are calculated and their Area/S_{BET} values are ranked in the

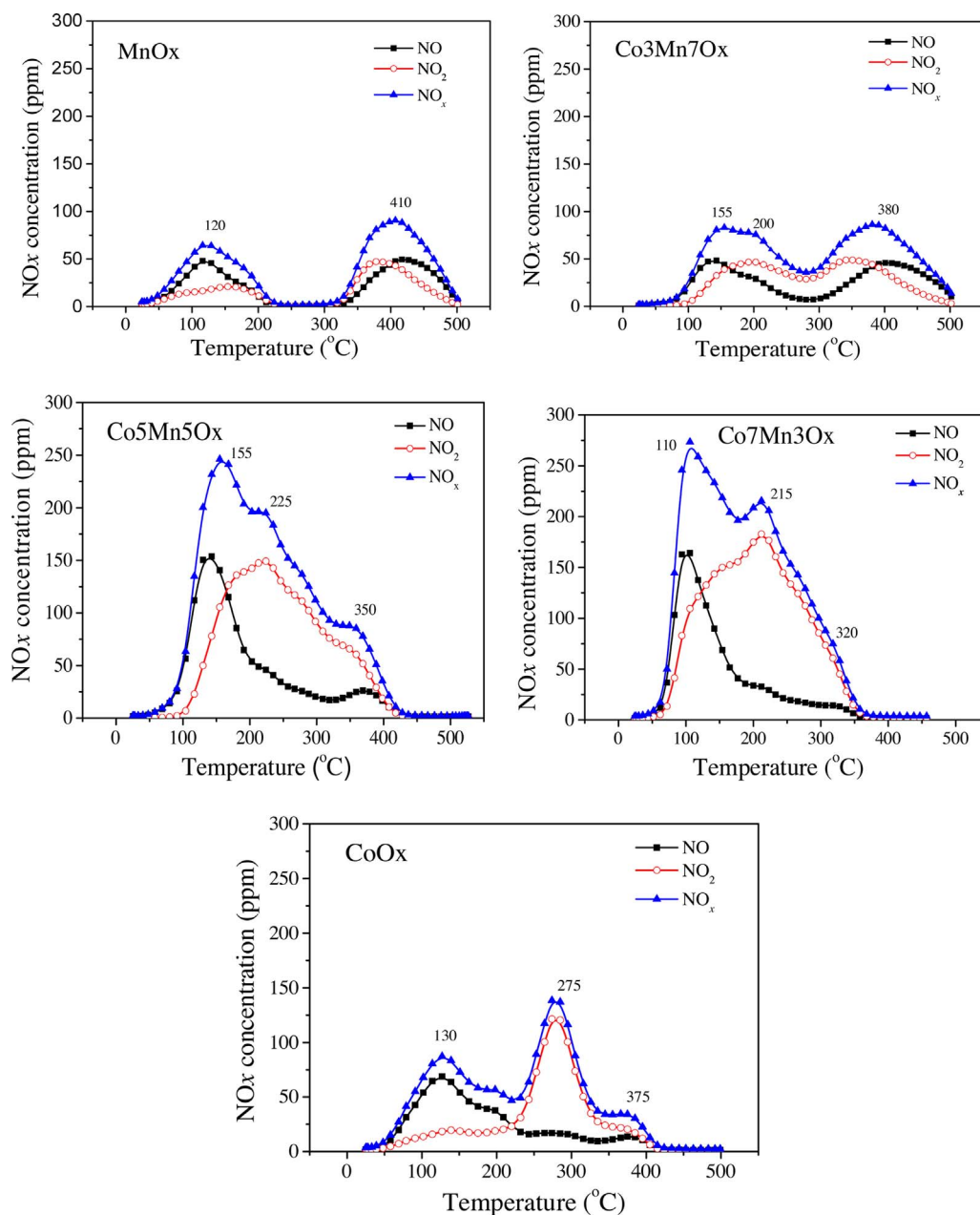


Fig. 15. NO_x-TPD profiles of the CoO_x, MnO_x and Co_aMn_bO_x catalysts after being treated in 500 ppm NO/5% O₂/Ar (300 mL/min) for 1 h.

order of CoO_x (10.0 μmol/m²) > Co₃Mn₇O_x (5.5 μmol/m²) > MnO_x (4.4 μmol/m²) ≈ Co₇Mn₃O_x (4.2 μmol/m²). This means that not only the specific surface area but also the Co_aMn_bO_x phases in the catalyst can influence the NO_x adsorption ability of the catalyst.

3.6. In situ DRIFT spectroscopy

All catalysts were first pretreated in Ar (50 mL/min) at 300 °C for 2 h and then cooled to 50 °C. Subsequently, the catalyst was exposed to a gas mixture of 500 ppm NO + 5 vol.% O₂/Ar (50 mL/min) at 50 °C, while in situ DRIFT spectra of the catalysts were taken at different times, and are shown in Fig. 16. There are many weak IR absorption bands at 1621, 1434, 1302 and 1215 cm⁻¹ in the spectrum of MnO_x and absorption bands at 1458 and 1325 cm⁻¹ in the spectrum of CoO_x. The absorption bands at 1621 cm⁻¹ can be attributed to bridged nitrates, and the absorption bands at 1325 and 1302 cm⁻¹ can be attributed to bidentate nitrates [49,50]. The band at 1215 cm⁻¹ indicates the existence of bridged nitrites [4,48,51], and the absorption bands at 1434 and 1458 cm⁻¹ belong to ionic nitrates [49]. After Co was added

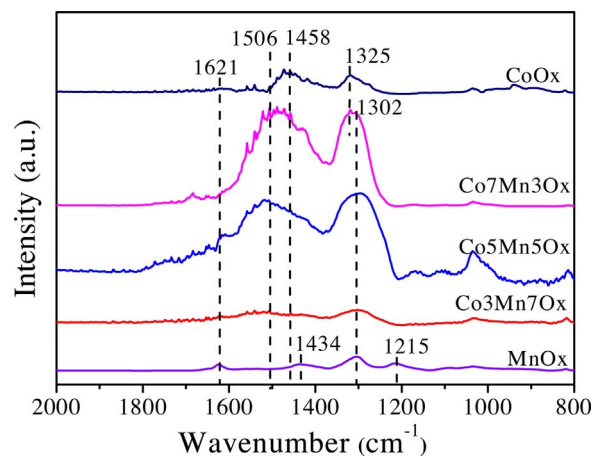


Fig. 16. In situ DRIFT spectra of the CoO_x, MnO_x and Co_aMn_bO_x catalysts in the mixed gas of 500 ppm NO + 5 vol.% O₂/Ar (50 mL/min) at 50 °C for 60 min.

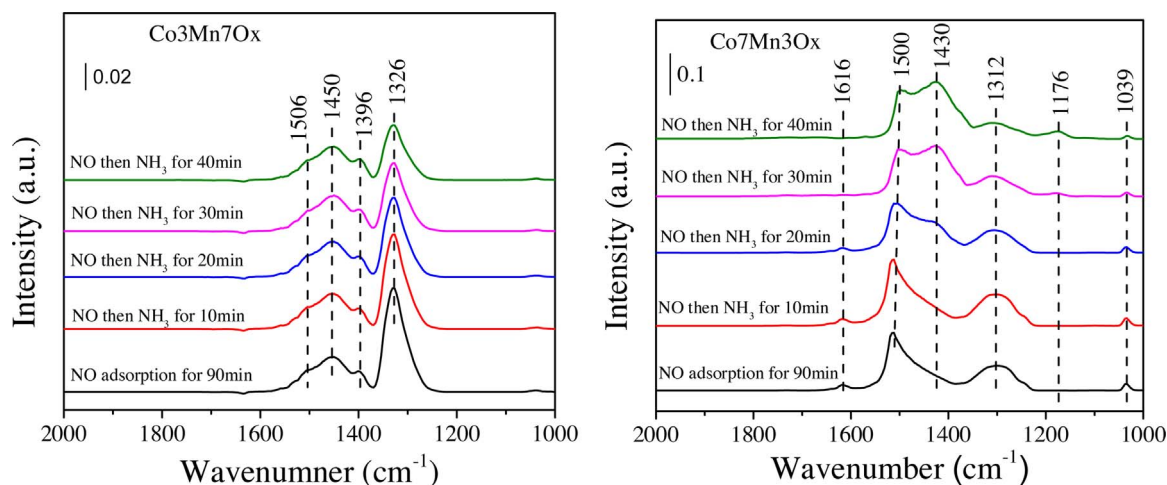


Fig. 17. In situ DRIFT spectra of the $\text{Co}_3\text{Mn}_7\text{O}_x$ and $\text{Co}_7\text{Mn}_3\text{O}_x$ catalysts in the mixed gas of 500 ppm NH_3/Ar for different times at 100°C after adsorption of 500 ppm $\text{NO} + 5 \text{ vol.}\% \text{O}_2/\text{Ar}$ at 100°C for 90 min and blowing of Ar for 1 h.

into MnO_x , it can be seen that in situ DRIFT spectra of the $\text{Co}_a\text{Mn}_b\text{O}_x$ catalysts were markedly influenced by the molar ratio of Co/Mn . The $\text{Co}_3\text{Mn}_7\text{O}_x$ catalyst exhibits two very weak absorption bands at 1506 and 1302 cm^{-1} , and the former absorption band is assigned to bidentate nitrate [52–54]. With increasing Co content, the intensity of the IR absorption bands greatly increased, as seen in the IR spectra of the $\text{Co}_5\text{Mn}_5\text{O}_x$ and $\text{Co}_7\text{Mn}_3\text{O}_x$ catalysts. These results indicate that the $\text{Co}_5\text{Mn}_5\text{O}_x$ and $\text{Co}_7\text{Mn}_3\text{O}_x$ catalysts have a much higher ability for forming nitrate species compared with the MnO_x , CoO_x and $\text{Co}_3\text{Mn}_7\text{O}_x$ catalysts, which is consistent with the NO_x -TPD results.

In order to study the reactivity of adsorbed nitrate/nitrite species, after the catalyst was exposed to the mixed gas of 500 ppm $\text{NO} + 5 \text{ vol.}\% \text{O}_2/\text{Ar}$ (50 mL/min) at 100°C for 90 min, Ar (50 mL/min) was first introduced to sweep the catalysts for 1 h and then replaced by 500 ppm NH_3/Ar at 100°C . The in situ DRIFT spectra of the catalysts were collected at different times, as shown in Fig. 17. The results revealed that in the in situ DRIFT spectra of the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst, the intensity of the band at 1326 cm^{-1} assigned to bidentate nitrate decreased with an increase in the exposure time of NH_3 , indicating that bidentate nitrates are the reactive species for the SCR reaction. In contrary, the intensity of the band at 1450 cm^{-1} assigned to ionic nitrate is hardly changed with an increase in the exposure time of NH_3 , indicating that ionic nitrate are inactive in the SCR reaction. In the in situ DRIFT spectra of the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst, the intensity of the band at 1616 cm^{-1} assigned to bridged nitrate, and the bands at 1500 and 1312 cm^{-1} assigned to bidentate nitrate decreased with an increase in the exposure time of NH_3 , indicating that both bridged and bidentate nitrates are the reactive species for the SCR reaction. Moreover, the decrease in the intensity of the bands is more distinct in the spectra of the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst compared with that of the $\text{Co}_3\text{Mn}_7\text{O}_x$ catalyst, thus suggesting that the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst possesses a high activity. On the other hand, in the in situ DRIFT spectra of the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst, the bands at 1430 and 1176 cm^{-1} assigned to NH_4^+ ions formed on Brønsted acid sites [55–57], and coordinated NH_3 adsorbed at Lewis acid sites [55,56,58] respectively, appeared and increased with the increase in the exposure time of NH_3 . In contrary, at prolonged NH_3 exposure times, seldom new peaks emerged in the spectrum of the $\text{Co}_3\text{Mn}_7\text{O}_x$ catalyst, indicating that the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst has a higher ability for NH_3 adsorption. These results are in good agreement with the NH_3 -TPD results.

To explore the reaction scheme in depth, the reaction of NH_3 species adsorbed on the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst surface in advance with the mixed gas of $\text{NO} + \text{O}_2$ was also conducted and the results are shown in Fig. 18. The $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst were first pretreated in Ar (50 mL/min) at 300°C for 2 h and then cooled to 50°C . Subsequently, the catalyst was exposed to 500 ppm NH_3/Ar (50 mL/min) at 50°C , while in situ

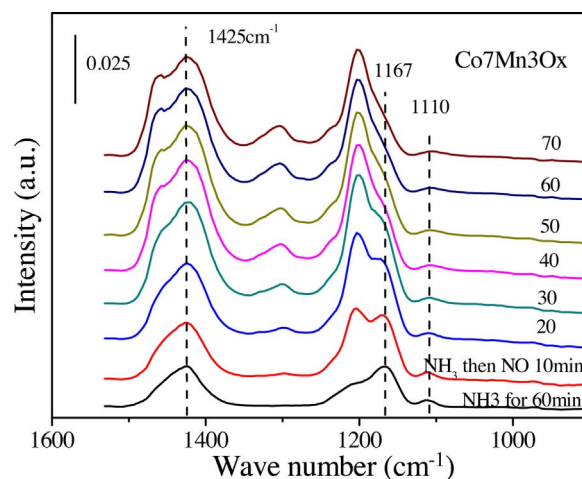
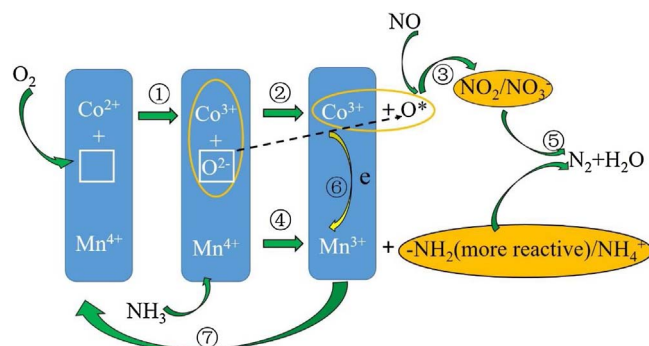


Fig. 18. In situ DRIFT spectra of the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst in the mixed gas of 500 ppm $\text{NO} + 5 \text{ vol.}\% \text{O}_2/\text{Ar}$ for different times after adsorption of 500 ppm NH_3/Ar at 50°C and blowing of Ar for 1 h.

DRIFT spectra of the catalysts were taken at different times. As shown in Fig. 18, after NH_3 adsorption on the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst for 1 h, there are mainly three IR absorption bands at 1425, 1167 and 1110 cm^{-1} in the spectrum of the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst. The former can be attributed to NH_4^+ ions formed on Brønsted acid sites [55–57], and the latter two can be attributed to coordinated NH_3 adsorbed at Lewis acid sites [55,56,58]. After the experiments of NH_3 adsorption on the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst were performed, Ar (50 mL/min) was first introduced to sweep the catalysts at 50°C for 1 h and was then replaced by 500 ppm $\text{NO} + 5 \text{ vol.}\% \text{O}_2/\text{Ar}$ (50 mL/min), while in situ DRIFT spectra of the catalysts were collected at different times. As shown in Fig. 18, the bands at 1167 and 1110 cm^{-1} disappeared gradually with the increase in the exposure time of $\text{NO} + \text{O}_2$, which indicate that coordinated NH_3 adsorbed at Lewis acid sites have taken part in the SCR process. On the contrary, the bands at 1425 cm^{-1} increased with the increase of the exposure time in $\text{NO} + \text{O}_2$ due to the overlap in the signals of nitrite species and NH_4^+ ions formed on Brønsted acid sites in this region. Therefore, the reactivity of NH_4^+ ions formed on Brønsted acid sites is still a mystery.

4. Discussion

It was reported that MnO_x has a high activity for NH_3 -SCR at low temperature [14,34,35]. However, its thermal stability is poor [15,48]. Herein, a series of $\text{Co}_a\text{Mn}_b\text{O}_x$ mixed oxides were prepared by the co-



Scheme 1. The proposed mechanism of the NH_3 -SCR reaction over the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst and the synergetic catalytic effect between Mn and Co cations.

precipitation method to develop a highly efficient NH_3 -SCR catalyst along with a high thermal stability. The results show that the combination of Mn and Co to form a mixed oxide can dramatically enhance the NH_3 -SCR activity, and the activity of $\text{Co}_a\text{Mn}_b\text{O}_x$ mixed oxides is dependent on the Co/Mn molar ratio. The apparent energy barrier of $\text{Co}_3\text{Mn}_7\text{O}_x$ (19.3 kJ/mol), $\text{Co}_5\text{Mn}_5\text{O}_x$ (18.8 kJ/mol) and $\text{Co}_7\text{Mn}_3\text{O}_x$ (15.7 kJ/mol) are significantly lower than that of MnO_x (33.9 kJ/mol) and CoO_x (24.3 kJ/mol), and the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst possessed the best NH_3 -SCR activity with an operation temperature window (80% NO_x conversion) of 116–285 °C. Furthermore, the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst exhibited a higher thermal stability, as well as excellent water- and sulfur-resistance performance compared with MnO_x .

The crystal structure, phase state and specific surface area between the $\text{Co}_a\text{Mn}_b\text{O}_x$ and MnO_x catalysts is significantly different, and those of the $\text{Co}_a\text{Mn}_b\text{O}_x$ catalysts are influenced by the composition. The $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst exhibited a large specific surface area due to its small particle size. As a result, the $\text{Co}_a\text{Mn}_b\text{O}_x$ catalysts possessed the high NH_3 and NO_x adsorption ability, especially the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst, which is beneficial to the high catalytic activity of the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst in NH_3 -SCR. Furthermore, the NO_x and NH_3 species formed on the $\text{Co}_a\text{Mn}_b\text{O}_x$ catalyst are different from that on MnO_x and CoO_x catalyst after the adsorption of NO_x and NH_3 . Different NO_x and NH_3 species generally played varied roles and have different performance in NH_3 -SCR reaction, leading to a significant improvement in SCR activity of the $\text{Co}_a\text{Mn}_b\text{O}_x$ catalyst [47,48]. On the other hand, the reducibility of the $\text{Co}_a\text{Mn}_b\text{O}_x$ catalysts is much better than those of the MnO_x and CoO_x catalysts. Moreover, the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst has better oxygen mobility than MnO_x , and consumed lattice oxygen can be quickly replenished by gaseous oxygen. In contrary, the $\text{Co}_3\text{Mn}_7\text{O}_x$, $\text{Co}_5\text{Mn}_5\text{O}_x$ and $\text{Co}_7\text{Mn}_3\text{O}_x$ catalysts exhibited similar reducibility at low temperature (< 400 °C). Therefore, the $\text{Co}_a\text{Mn}_b\text{O}_x$ catalysts exhibited similar catalytic activities for NO oxidation at low temperature (< 200 °C), but are higher than those of the MnO_x and CoO_x catalysts. The high catalytic activity for NO oxidation can prompt the “fast SCR” reaction ($\text{NO} + \text{NO}_2 + 2\text{NH}_3 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}$), leading to the increase in the NH_3 -SCR activity of the $\text{Co}_a\text{Mn}_b\text{O}_x$ catalysts.

As for the reaction mechanism, NO_x species could adsorb on the surface of the $\text{Co}_a\text{Mn}_b\text{O}_x$ and MnO_x catalysts in the different form. Bidentate nitrate is dominant on the $\text{Co}_a\text{Mn}_b\text{O}_x$ catalyst, while bridged nitrate on the MnO_x catalysts. Moreover, the $\text{Co}_5\text{Mn}_5\text{O}_x$ and $\text{Co}_7\text{Mn}_3\text{O}_x$ catalysts have a much higher ability for forming nitrate species compared with the MnO_x and $\text{Co}_3\text{Mn}_7\text{O}_x$ catalysts. Both bidentate and bridged nitrates are the reactive species for the SCR reaction, whereas ionic nitrate are inactive in the SCR reaction. On the hand, coordinated NH_3 adsorbed at Lewis acid sites have been confirmed to take part in the SCR process. In contrary, the reactivity of NH_4^+ ions formed on Brønsted acid sites is still a mystery, due to the overlap in the signals of nitrite species and NH_4^+ ions formed on Brønsted acid sites in situ DRIFT spectra.

Based on these abovementioned results, the reaction pathway of

NH_3 -SCR over the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst can be proposed as shown in Scheme 1. Gaseous oxygen can be adsorbed and activated on oxygen vacancies (symbol \square) and can be transformed into lattice oxygen O^{2-} (Step 1), which can diffuse to the catalyst surface and act as surface active oxygen (O^*) during the SCR reaction (Step 2). Gaseous NO is adsorbed and then oxidized to $\text{NO}_2/\text{NO}_3^-$ by O^* (Step 3), while NH_3 is activated by Mn^{4+} to form $-\text{NH}_2$ (higher activity confirmed by in situ DRIFT) and NH_4^+ (Step 4). Finally, $\text{NO}_2/\text{NO}_3^-$ reacts with the NH species to produce N_2 and H_2O (Step 5). The transformed Co^{3+} and Mn^{3+} are recovered by electron transfer (Step 6) and return to their original state (Step 7).

5. Conclusions

$\text{Co}_a\text{Mn}_b\text{O}_x$ catalysts prepared by the co-precipitation method were developed for NH_3 -SCR. The $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst with a Co/Mn molar ratio of 7/3 exhibited the optimal catalytic activity at low temperature, over which NO_x conversion is greater than 80% at 116–285 °C. The apparent activation energy of the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst was much smaller than that of MnO_x , indicating that the active sites on the MnO_x surface were altered due to the introduction of cobalt. In addition, the presence of cobalt can also enhance the thermal stability and the SO_2 and/or H_2O resistance of MnO_x . For instance, 5% H_2O in the reactant gas has little influence on the activity of the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst, and 62% NO can be removed after being poisoned by 50 ppm SO_2 for nearly 10 h. The deactivated catalysts can be totally regenerated by simply washing with water.

The $\text{Co}_a\text{Mn}_b\text{O}_x$ catalysts possess improved redox properties and more surface acid sites than either MnO_x or CoO_x alone due to synergistic effects between the Co and Mn species. In comparison with other $\text{Co}_a\text{Mn}_b\text{O}_x$ catalysts, the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst has a higher adsorption ability for NH_3 and $\text{NO} + \text{O}_2$, which is ascribed to the $\text{MnCo}_2\text{O}_{4.5}$ phase and the higher surface area. Furthermore, the results of in situ DRIFT indicated that bridging nitrate and bidentate nitrate are the intermediate species in NH_3 -SCR. The high adsorption ability for $\text{NO} + \text{O}_2$ and improved redox properties of the $\text{Co}_7\text{Mn}_3\text{O}_x$ catalyst are beneficial for the formation of nitrate species on the catalyst surface to result in high SCR activity.

Acknowledgments

This work was financially supported by the National Key Research and Development Program of China (2016YFC0204300), the National Key Basic Research Program of China (2013CB933200), the National Natural Science Foundation of China (21577034, 21333003), Science and Technology Commission of Shanghai Municipality (16ZR1407900) and Fundamental Research Funds for the Central Universities (WJ1514020, 222201717003).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2017.09.034>.

References

- [1] D. Kwon, K. Nam, S. Hong, Appl. Catal. B Environ. 166–167 (2015) 37–44.
- [2] C. D’Agostino, S. Chansai, I. Bush, C. Gao, M.D. Mantle, C. Hardacre, S.L. James, L.F. Gladden, Catal. Sci. Technol. 6 (2015) 1661–1666.
- [3] V. Parvulescu, P. Grange, B. Delmon, Catal. Today 46 (1998) 233–316.
- [4] Z. Xiong, C. Wu, Q. Hu, H.Z. Wang, J. Jin, C.M. Liu, D.X. Guo, Chem. Eng. J. 286 (2016) 459–466.
- [5] N.Y. Topsøe, Science 265 (1994) 1217–1219.
- [6] T.J. Toops, J.A. Pihl, W.P. Partridge, Fe-zeolite functionality, durability, and deactivation mechanisms in the selective catalytic reduction (SCR) of NO_x with ammonia, in: I. Nova, E. Tronconi (Eds.), Urea-SCR Technology for De NO_x After Treatment of Diesel Exhausts, Springer, New York, 2014, pp. 97–122.
- [7] J.H. Park, H.J. Park, J.H. Bak, I.S. Nam, C.H. Shin, J.H. Lee, B.K. Cho, S.H. Oh, J.

- Catal. 240 (2006) 47–57.
- [8] T.V.W. Janssens, H. Falsig, L.F. Lundegaard, P.N.R. Vennestrøm, S.B. Rasmussen, P.G. Moses, F. Giordano, E. Borfecchia, K.A. Lomachenko, C. Lamberti, S. Bordiga, A. Godiksen, S. Mossin, P. Beato, ACS Catal. 5 (2015) 2832–2845.
 - [9] L. Sun, Q. Cao, B. Hu, J. Li, J. Hao, G. Jing, X. Tang, Appl. Catal. A Gen. 393 (2011) 323–330.
 - [10] M. Kang, E.D. Park, J.M. Kim, J.E. Yie, Catal. Today 111 (2006) 236–241.
 - [11] C. Zhou, Y. Zhang, X. Wang, H. Xu, K. Sun, K. Shen, J. Colloid Interface Sci. 392 (2013) 319–324.
 - [12] S. Roy, B. Viswanath, M. Hegde, G. Madras, J. Phys. Chem. C 112 (2008) 6002–6012.
 - [13] D.A. Peña, B.S. Uphade, P.G. Smirniotis, J. Catal. 221 (2004) 421–431.
 - [14] M. Kang, E.D. Park, J.M. Kim, J.E. Yie, Appl. Catal. A Gen. 327 (2007) 261–269.
 - [15] D. Meng, W. Zhan, Y. Guo, Y. Guo, L. Wang, G. Lu, J. Mol. Catal. A Chem. 420 (2016) 272–281.
 - [16] W. Tian, H.S. Yang, X.Y. Fu, X.B. Zhang, J. Hazard. Mater. 188 (2011) 105–109.
 - [17] B. Meng, Z. Zhao, X. Wang, J. Liang, J. Qiu, Appl. Catal. B Environ. 129 (2013) 491–500.
 - [18] J.E. Park, E.D. Park, Catal. Lett. 144 (2014) 607–614.
 - [19] Y. Yan, L. Wang, H. Zhang, Sep. Purif. Technol. 175 (2017) 213–221.
 - [20] C. Zhang, C. Wang, W. Zhan, Y. Guo, Y. Guo, G. Lu, A. Baylet, A. Giroir-Fendler, Appl. Catal. B Environ. 129 (2013) 509–516.
 - [21] W. Tang, X. Wu, S. Li, W. Li, Y. Chen, Cat. Commun. 56 (2014) 134–138.
 - [22] W. Li, K. Xu, G. Song, X. Zhou, R. Zou, J. Yang, Z. Chen, J. Hu, Cryst. Eng. Commun. 16 (2014) 2335–2339.
 - [23] Y. Lu, W. Zhan, Y. He, Y. Wang, X. Kong, Q. Kuang, Z. Xie, L. Zheng, ACS Appl. Mater. Interfaces 6 (2014) 4186–4195.
 - [24] H. Zhou, L. Chen, V. Malik, C. Knies, D.M. Hofmann, K.P. Bhatti, S. Chaudhary, P.J. Klar, W. Heimbrod, C. Klingshirn, Phys. Status Solidi (A) 204 (2007) 112–117.
 - [25] M. Richter, A. Trunschke, U. Bentrup, K.W. Brzezinka, E. Schreier, M. Schneider, M.M. Pohl, R. Fricke, J. Catal. 206 (2002) 98–113.
 - [26] R. Radhakrishnan, S.T. Oyama, J. Catal. 199 (2001) 282–290.
 - [27] Y.F. Han, K. Ramesh, L. Chen, E. Widjaja, S. Chilukoti, F. Che, J. Phys. Chem. C 111 (2007) 2830–2833.
 - [28] B. Fazio, L. Spadaro, G. Trunfio, J. Negro, F. Arena, J. Raman Spectrosc. 42 (2011) 1583–1588.
 - [29] Z. Chen, Q. Yang, H. Li, X. Li, L. Wang, S. Chi Tsang, J. Catal. 276 (2010) 56–65.
 - [30] H.-S. Kim, P.C. Stair, J. Phys. Chem. B 108 (2004) 17019–17026.
 - [31] Y.L. Zheng, W.Z. Wang, D. Jing, L. Zhang, Chem. Eng. J. 284 (2016) 21–27.
 - [32] X. Tang, J. Li, L. Sun, J. Hao, Appl. Catal. B Environ. 99 (2010) 156–162.
 - [33] L. Zhang, L. Shi, L. Huang, J. Zhang, R. Gao, D. Zhang, ACS Catal. 4 (2014) 1753–1763.
 - [34] S. Yang, C. Wang, J. Li, N. Yan, L. Ma, H. Chang, Appl. Catal. B Environ. 110 (2011) 71–80.
 - [35] J. Chen, M. Shen, X. Wang, G. Qi, J. Wang, W. Li, Appl. Catal. B Environ. 134–135 (2013) 251–257.
 - [36] D. Li, X. Liu, Q. Zhang, Y. Wang, H. Wan, Catal. Lett. 127 (2009) 377–385.
 - [37] Z. Lian, F. Liu, H. He, X. Shi, J. Mo, Z. Wu, Chem. Eng. J. 250 (2014) 390–398.
 - [38] Y.X. Su, B.X. Fan, L.S. Wang, Y.F. Liu, B.C. Huang, M.L. Fu, L.M. Chen, D.Q. Ye, Catal. Today 201 (2013) 115–121.
 - [39] Z.Q. Zou, M. Meng, Y.Q. Zha, J. Phys. Chem. C 114 (2010) 468–477.
 - [40] X.F. Tang, Y.G. Li, X.M. Huang, Y.D. Xu, H.Q. Zhu, J.G. Wang, W.J. Shen, Appl. Catal. B Environ. 62 (2006) 265–273.
 - [41] F. Kapteijn, L. Singoredjo, A. Andreini, J.A. Moulijn, Appl. Catal. B Environ. 25 (1994) 173–189.
 - [42] M.Z. Wu, W.C. Zhan, Y.L. Guo, Y. Guo, Y.S. Wang, L. Wang, G.Z. Lu, Appl. Catal. A Gen. 523 (2016) 97–106.
 - [43] A. Patel, P. Shukla, J.L. Chen, T.E. Rufford, V. Rudolph, Z.Z. Zhu, Catal. Today 212 (2013) 38–44.
 - [44] R.B. Jin, Y. Liu, Y. Wang, W.L. Cen, Z.B. Wu, H.Q. Wang, X.L. Weng, Appl. Catal. B Environ. 148–149 (2014) 582–588.
 - [45] M. Ruggeri, I. Nova, E. Tronconi, J.A. Pihl, T.J. Toops, W.P. Partridge, Appl. Catal. B Environ. 166–167 (2015) 181–192.
 - [46] H. Xu, Q. Zhang, C. Qiu, T. Lin, M. Gong, Y. Chen, Chem. Eng. Sci. 76 (2012) 120–128.
 - [47] F. Liu, H. He, Y. Ding, C. Zhang, Appl. Catal. B Environ. 93 (2009) 194–204.
 - [48] D. Meng, W. Zhan, Y. Guo, Y. Guo, L. Wang, G. Lu, ACS Catal. 5 (2015) 5973–5983.
 - [49] Q. Li, M. Meng, Z.-Q. Zou, X.-G. Li, Y.-Q. Zha, J. Hazard. Mater. 161 (2009) 366–372.
 - [50] S.M. Lee, S.C. Hong, Appl. Catal. B 163 (2015) 30–39.
 - [51] S. Liu, X.D. Wu, D. Weng, R. Ran, Ind. Eng. Chem. Res. 51 (2012) 2271–2279.
 - [52] I. Atribak, B. Azambre, A. Bueno López, A. García-García, Appl. Catal. B Environ. 92 (2009) 126–137.
 - [53] Z. Zhang, Y. Zhang, Q. Su, Z. Wang, Q. Li, X. Gao, Environ. Sci. Technol. 44 (2010) 8254–8258.
 - [54] G. Qi, R.T. Yang, J. Phys. Chem. B 108 (2004) 15738–15747.
 - [55] F. Liu, H. He, J. Phys. Chem. C 114 (2010) 16929–16936.
 - [56] D.A. Peña, B.S. Uphade, E.P. Reddy, P.G. Smirniotis, J. Phys. Chem. B 108 (2004) 9927–9936.
 - [57] N. Topsoe, H. Topsoe, J. Dumesic, J. Catal. 151 (1995) 226–240.
 - [58] H.K. Matralis, M. Ciardelli, M. Ruwet, P. Grange, J. Catal. 157 (1995) 368–379.